OPTIMIZATION OF CHEMICAL AND ENZYMATIC DEINKING OF PHOTOCOPIER WASTE PAPER

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The utilization of post-consumer papers in the production of new paper products is increasing all over the world in recent years. Recycling of photocopier paper is a major problem due to difficulty in removal of non-impact ink. Enzymes offer potential advantages in ecofriendly deinking of recovered paper. In this study the deinking of photocopier paper was examined using chemicals and a commercial cellulase enzyme. Parameters of deinking experiments were optimized for hydrapulping. The ink was removed by flotation and washing processes. Then these parameters were compared in terms of ink removal ability of the process, as well as optical and strength properties of the deinked paper. The application of enzymatic deinking improved ink removal efficiency by 24.6% and freeness by 21.6% with a reduction in drainage time of 11.5% in comparison to those obtained with chemical deinking. The physical properties, namely burst index and tensile index, were observed to improve by 15.3% and 2.7%, respectively and brightness and tear index decreased by 2.1% and 21.9%, respectively. Results of deinking efficiency of photocopier paper showed that the enzyme used in the present work performed better than the conventional chemicals used for deinking.

Keywords: Photocopier paper; Deinking; Cellulase; Deinking efficiency; ISO brightness; Residual ink.

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INTRODUCTION

The pulp and paper manufacturing industry is one of the largest consumers of wood today. Along with increasing world economic growth, a substantial increase in paper consumption is expected. As a result, due to more harvesting of trees, the paper industry could well experience a limited raw material resource, with concurrent reduction of industry growth. Therefore, "recycling of paper", as a solution to this problem, is attracting more and more attention. It offers an effective way to preserve forest resources and save energy and landfill space. Furthermore, papermakers are focusing on recycling as an economic necessity.

One of the important processes in recycling of paper is the deinking i.e. the removal of the printing ink from the used paper to obtain brighter pulp. The process of deinking involves ink particles' dislodgement from the fiber surface and the separation of the dispersed ink from fiber suspensions by washing or flotation (Bajpai and Bajpai 1998; Prasad *et al.*1993). The efficiency of this method depends on the technique, printing conditions, kind of ink, and kind of printing substrate. The photocopier printers use thermosetting toners, consisting of non-dispersible synthetic polymers, as ink for printing

the paper. This ink is physically bonded to the fibers because of high heat, making it difficult and expensive to remove by conventional chemical methods (Jefferies *et al.* 1993; Woodward *et al.* 1994). Most of the conventional deinking techniques require large amounts of chemical agents, such as sodium hydroxide, sodium carbonate, diethylenetriaminepentacetic acid, sodium silicate, hydrogen peroxide, and surfactants (Prasad *et al.* 1993; Putz *et al.* 1994), resulting in a costly wastewater treatment to meet the environmental regulations. Enzyme usage has been reported to be a potentially efficient and less polluting solution to overcome this disposal problem (Prasad *et al.*1993; Ladisch *et al.*1983).

Several enzymes such as cellulases, hemicellulases, pectinase, lipase, esterase, α-amylase, and lignolytic enzymes have been used for deinking of various waste papers. In most cases cellulases and hemicellulases have been used, whereas others have been used only for some specific purposes, e.g. in case of paper printed with oil based inks, paper with starch coating, etc. (Bajpai and Bajpai 1998). The mechanism by which cellulase can improve the deinkability of waste paper is widely discussed in the literature (Prasad *et al.*1992, 1993; Jeffries *et al.*1996; Pathak *et al.*2010). A general understanding is that cellulases dislodge inks by peeling off fibers or fines on paper surfaces (Welt *et al.*1995; Bajpai 1997). In one of the studies, Vidotti *et al.*(1995) proposed that hydrolysis of fibrils attached to toner ink particles reduces the hydrodynamic volume or hydrodynamic size of the toner particles/fiber agglomerate and increases the hydrophobicity of the particles, which both aid in flotation deinking efficiency.

Most of the cited studies reported the deinking of Mixed Office Waste (MOW), consisting of photocopier papers with other type of papers, by using commercially available enzymes. Our aim is to investigate the deinking of photocopier paper alone by using (i) conventional chemicals as control versus (ii) commercial cellulase enzyme. The present paper reports our investigation on conventional chemical and enzymatic deinking using commercial enzyme. We assayed conventional chemicals and commercially available cellulase to optimize the parameters that determine the maximum ink removal, with minimum possible deterioration of fiber, on photocopier paper.

MATERIALS AND METHODS

Chemicals, Enzyme and Waste Papers

The chemicals used in present investigation were procured from Qualigens Fine Chemicals (Fischer Scientific-AR Grade) and Himedia Laboratories Pvt. Ltd. (AR Grade). Commercial cellulase OPTIMASE™ CX 40L (*Trichoderma viridae*) used for deinking was obtained from Genencor International, New York. The enzyme was stored at 4°C prior to use. This enzyme acts mainly on the surface of the fiber in the acidic to neutral pH range (pH 4.0 to 7.0) and between temperatures of 40 and 65°C. The cellulase activity was measured using the carboxymethyl cellulase (CMCase) method (Mandels *et al.* 1976). Its highest activity was found to be 991 IU/mL at 50°C and pH 5.8. Copier paper (sheet size 210x297mm, basis weight 75 gsm) from an Indian mill was used to produce photocopier waste paper after printing with Xerox Black Toner, 6R1046 (Part # 006R01046) used for Xerox Workcenter 238 photocopier machine. To reduce the

variables in comparing repulping and flotation results, one set of ‘‘standard’’ printed sheets was prepared and used for all the trials performed in this work.

Optimization Procedure

The variables for chemical as well as enzymatic deinking were optimized one at a time, while other variables were fixed. For the optimization of chemical deinking process parameters we set our experiments according to Table 1. First of all the optimization of NaOH was done. This was followed by experiments to optimize of time, temperature, Na_2SiO_3, H_2O_2, consistency, and oleic acid.

Table 1. Pulping Process Parameter Variables for Optimization of Chemical Deinking

Optimization parameters	Exp. No.	NaOH (%)	Hydrapulping time (minute)	Temperature (°C)	Na_2SiO_3 (%)	H_2O_2 (%)	Consistency (%)	Oleic acid (%)#	DTPA (%)	End pH ± 0.1 (Hydra-pulping)	End pH ± 0.1 (Flotation)
NaOH	**C1**	**1.5**	30	70	2	1	6	0.8	0.8	10	8
	C2	**2**	30	70	2	1	6	0.8	0.8	10.4	8.6
	C3	**2.5**	30	70	2	1	6	0.8	0.8	10.9	9
Hydrapulping time	**C4**	2	**20**	70	2	1	6	0.8	0.8	10.4	8.5
	C2	2	**30**	70	2	1	6	0.8	0.8	10.5	8.5
	C5	2	**40**	70	2	1	6	0.8	0.8	10.5	8.4
Temperature	**C7**	2	30	**65**	2	1	6	0.8	0.8	10.5	8.4
	C2	2	30	**70**	2	1	6	0.8	0.8	10.5	8.5
	C8	2	30	**75**	2	1	6	0.8	0.8	10.5	8.5
Na_2SiO_3	**C9**	2	30	70	**1**	1	6	0.8	0.8	10.5	8.4
	C10	2	30	70	**1.5**	1	6	0.8	0.8	10.5	8.5
	C2	2	30	70	**2**	1	6	0.8	0.8	10.5	8.5
	C11	2	30	70	**2.5**	1	6	0.8	0.8	10.5	8.5
H_2O_2	**C12**	2	30	70	2	**0.5**	6	0.8	0.8	10.5	8.4
	C2	2	30	70	2	**1**	6	0.8	0.8	10.5	8.5
	C13	2	30	70	2	**1.5**	6	0.8	0.8	10.5	8.6
Consistency	**C2**	2	30	70	2	1	**6**	0.8	0.8	10.5	8.5
	C14	2	30	70	2	1	**8**	0.8	0.8	10.5	8.4
	C15	2	30	70	2	1	**10**	0.8	0.8	10.5	8.4
	C16	2	30	70	2	1	**12**	0.8	0.8	10.5	8.4
Oleic acid	**C17**	2	30	70	2	1	10	**0.6**	0.8	10.5	8.4
	C15	2	30	70	2	1	10	**0.8**	0.8	10.5	8.3
	C18	2	30	70	2	1	10	**1**	0.8	10.5	8.6

Half (50%) of the oleic acid was added during the hydrapulping and 50% was added during the flotation stage.

For the optimization of NaOH, the values of NaOH were varied, and all other parameters were kept constant. Then a dose of NaOH was chosen with the aim of obtaining higher deinking efficiency, ISO brightness, and lower residual ink. Then, by keeping this selected value of NaOH fixed, the values of next parameter, i.e. time, were varied while keeping the other parameters constant. Similarly, optimization of the remaining parameters was carried out. Enzymatic deinking process parameters were optimized according to Table 2. Optimization of enzyme dose was followed by the experiments for optimization of consistency and reaction time.

Table 2. Pulping Process Parameter Variables for Optimization of Enzymatic Deinking

Optimization parameters		Experiment No.	Enzyme dose (IU)	Consistency (%)	Reaction Time (minutes)	Hydrapulping time (min)	Temperature (°C)	Oleic acid (%)#	End pH ± 0.1 (Hydrapulping)	End pH ± 0.1 (Flotation)
Point of inocula-tion	**Before HP**	**E1**	500	10	90	30	50	0.8	5.8	6.7
	During HP	**E2**	500	10	90	30	50	0.8	5.8	6.7
	After HP	**E3**	500	10	90	30	50	0.8	5.8	6.7
Enzyme dose		**E2**	**500**	10	90	30	50	0.8	5.8	6.7
		E4	**1000**	10	90	30	50	0.8	5.8	6.7
		E5	**1500**	10	90	30	50	0.8	5.8	6.7
		E6	**2000**	10	90	30	50	0.8	5.8	6.7
		E7	**2500**	10	90	30	50	0.8	5.8	6.7
Consistency		**E8**	1500	**6**	90	30	50	0.8	5.8	6.7
		E9	1500	**8**	90	30	50	0.8	5.8	6.7
		E5	1500	**10**	90	30	50	0.8	5.8	6.7
		E10	1500	**12**	90	30	50	0.8	5.8	6.7
		E11	1500	**14**	90	30	50	0.8	5.8	6.7
Reaction time (including 30 minutes hydrapulping time)		**E12**	1500	10	**30**	30	50	0.8	5.8	6.7
		E13	1500	10	**60**	30	50	0.8	5.8	6.7
		E5	1500	10	**90**	30	50	0.8	5.8	6.7
		E14	1500	10	**120**	30	50	0.8	5.8	6.7
		E15	1500	10	**150**	30	50	0.8	5.8	6.7

Half (50%) of the oleic acid was added during the hydrapulping and 50% was added during the flotation stage.

Pulping and Flotation

The waste paper was manually torn into a size of approximately 1-inch squares. The repulping of 250 gm paper on an oven-dry basis was carried out at different chemical/enzyme dose, consistency, temperature, and time in hydrapulper (HP). The process variables are listed in **Tables 1 and 2.** The pH was maintained with sulphuric acid during the enzymatic deinking. For flotation, the pulp was diluted to approximately

1% consistency by using water. To separate toner particles from the fibers, all the treatments, whether chemical or enzymatic, were followed by a 10 min flotation run in a 25 litre capacity laboratory Voith flotation unit at 40±2 °C temperature. At the end of flotation, the deinked fibers were recovered on muslin cloth from the drain valve of the flotation cell. Then the pulp was agitated for 5 minutes by hand at 2% consistency in the bucket. After this, pulp was filtered on a screen. This washing process was repeated thrice.

Control runs were carried out under identical conditions without deinking chemicals for chemical deinking (Control[a] in Table 6) and replacing active enzyme by heat-denatured enzyme for enzymatic deinking (Control[b] in Table 6). Blank samples, meant for estimating total ink, were the pulp sample treated with chemicals and enzyme but not processed by flotation (Blank[a] and Blank[b] in Table 6).

The procedure using a Büchner funnel for preparing specimen sheets for reflectance testing of pulps was followed. Following TAPPI Test Method T 218 sp-97, the sheets were made at a pH of 6.5 ± 0.5. For determining the physical properties of pulp, TAPPI Test Method T 205 sp-95 was used to prepare handsheets. Fifteen handsheets per run (grammage 60 g/m^2) were made on a British handsheet maker unit, and the handsheets were conditioned at 27°C and 65% humidity. Handsheets from chemical treated, enzyme treated pulp, control runs, and blank runs were compared for different optical and strength properties. Freeness, drainage time, tensile index, burst index, double fold and tear index were determined using TAPPI standard tests T 227 om-99, T 221 cm-99, T 404 cm-92, T 403 om-97, T 511 om-96, and T 414 om-98, respectively. The related devices were of AB Lorentzen & Wettre make. Brightness, opacity, and Effective Residual Ink Concentration (ERIC) were measured, using an Elerpho-070/071 device at different places on each handsheet (TAPPI T 452 om-92). All the values were expressed as mean values, and the values reported after the ± sign in Tables 3, 4, and 6 are standard deviation at 95% level.

RESULTS AND DISCUSSION

Optimization of Chemical Deinking Parameters

For the optimization of chemical deinking, we selected a narrow range of parameters as reported by Wood *et al.* (1985). Accordingly, pH between 10 and 12, contact temperature between 50° C and 75° C, and hydrapulping time between 30 and 45 minutes were considered. The effect of chemical deinking on different pulp and paper properties is shown in Table 3.

Sodium hydroxide

Chemical doses of NaOH were optimized for the concentration of 1.5%, 2.0%, and 2.5%. For the 2.0% chemical dose, residual ink was lowest (118.54 ppm) and deinking efficiency was maximum (58.4%) with ISO brightness value of 78.68% (Fig. 1).

Hydrapulping time

The experiments were carried out with hydrapulping time of 20, 30, and 40 minutes. For 30 minutes hydrapulping time, deinking efficiency and ISO pulp brightness were maximum (58.4% and 78.68%, respectively) with lowest residual ink content (118.54 ppm) (Fig. 1).

Temperature

The optimization of temperature was considered for the temperatures 65°C, 70°C, and 75°C. The maximum deinking efficiency and brightness (58.4% and 78.68%, respectively) and minimum residual ink (118.54 ppm) were obtained for the 70°C (Fig. 1). Temperature beyond 70°C is considered to be unsuitable, as thermal reversion and accelerated alkali darkening can occur (Magnin 2002).

Sodium silicate

Chemical doses of the sodium silicate were optimized for the concentration of 1.0%, 1.5%, 2.0%, and 2.5%. The maximum deinking efficiency (58.4%) and ISO pulp brightness (78.68%) of paper sheets were obtained for 2.0% sodium silicate. Results show that residual ink was lowest (118.54 ppm) (Fig. 1).

H_2O_2

H_2O_2 doses were varied as 0.5%, 1.0%, and 1.5%. The maximum brightness (78.68%) and lowest residual ink (118.54 ppm) were achieved for the dose of 1.0% and maximum deinking efficiency obtained was 58.4% (Fig. 1).

Consistency

Pulp consistency was optimized from lower to medium, i.e. 6%, 8%, 10%, and 12%. The deinking efficiency and ISO brightness increased as the pulp consistency was increased. At yet higher consistency, it decreases. The highest deinking efficiency (75.93%) and ISO brightness, (80.38%) were achieved at 10% pulp consistency (Fig. 1). The relatively high consistency of 10% was chosen because it prompts fiber/ fiber attrition, favoring ink detachment; additionally, it would be advantageous for industrial usage.

Oleic acid

Oleic acid was added in the concentration range of 0.6%, 0.8%, and 1.0%. Half (50%) of the oleic acid was added during the hydrapulping and 50% was added during the flotation stage. Optimized dose was achieved for 0.8%, with maximum deinking efficiency (75.93%). On the other side, the yield was maximum for 0.6%, but due to low deinking efficiency it was not considered. Yield was 77.9% for the dose of 0.8% with maximum deinking efficiency (Fig. 1). Higher oleic acid dose resulted in higher pulp removal with the froth, so the net yield decreased.

Diethylene tri-amine penta acetic acid (DTPA)

The dose of DTPA was not optimized, because it is a chelating agent (to form soluble complex with heavy metals that prevents hydrogen peroxide decomposition).

Table 3. Effect of Chemical Deinking on the Pulp and Paper Properties

Parameters	Exp. No.	Yield (%)	CSF (ml)	Drainage rate (sec.)	Tensile Index (N.m/g)	Folding endurance	Burst index (kPa.m^2/g)	Tear index (mN.m^2/g)	Opacity (%)	Residual ink (ppm) (EP)#
NaOH	**C1**	76.7	458	7.17 ±0.63	24.8 ±5.85	0.756 ±0.1831	1.15 ±0.45	6.93 ± 0.68	90.53 ±0.57	256.45 ±5.65
	C2	77.1	500	6.63 ±0.31	31.49 ±2.75	0.8655 ±0.1283	1.45 ± 0.45	6.72 ±1.73	90.09 ±0.84	254.78 ±3.78
	C3	77.7	513	8.57 ±0.35	25.1 ±3.15	0.6937 ±3.15	0.96 ±0.42	6.43 ±1.2	91.47 ±0.71	249.54 ±3.87
Time	**C4**	77.3	480	9.25 ±0.49	30.77 ± 6.01	0.7484 ±0.1906	1.44 ±0.31	6.45 ±0.864	90.57 ±0.81	256.45 ±3.98
	C2	77.1	500	6.63 ±0.31	31.49 ±2.75	0.8655 ±0.1283	1.45 ± 0.45	6.72 ±1.73	90.09 ±0.84	254.78 ±3.78
	C5	77.2	520	7.29 ±0.32	31.21 ±3.61	0.9044 ±0.1301	1.86 ±0.16	6.38 ±1.32	91.31 ±0.88	251.67 ±5.87
Temp.	**C7**	77.6	480	6.23 ±0.30	29.62 ±3.25	0.8375 ±0.1546	1.56 ± 0.31	7.82 ±1.59	88.84 ±0.86	257.34 ±6.34
	C2	77.1	500	6.63 ±0.31	31.49 ±2.75	0.8655 ±0.1283	1.45 ± 0.45	6.72 ±1.73	90.09 ±0.84	254.78 ±3.78
	C8	76.0	470	7.07 ±0.15	28.83 ±3.98	0.8354 ±0.1199	1.47 ± 0.34	6.92 ±0.94	91.81 ±2.07	250.23 ±3.87
Na_2SiO_3	**C9**	79.3	484	6.74 ±0.47	28.45 ±4.22	0.8593 ±0.1893	1.73 ± 0.33	6.85 ±0.79	92.29 ±0.47	249.76 ±4.98
	C10	77.9	480	6.81 ±0.67	26.6 ±2.43	0.9422 ±0.0718	1.79 ± 0.30	6.98 ±0.91	91.58 ±0.58	250.45 ±6.98
	C2	77.1	500	6.63 ±0.31	31.49 ±2.75	0.8655 ±0.1283	1.45 ± 0.45	6.72 ±1.73	90.09 ±0.84	254.78 ±3.78
	C11	80.9	510	6.75 ±0.17	30.69 ±4.26	0.835 ±0.1250	1.65 ± 0.37	6.81 ±1.21	91.00 ±0.66	257.31 ±4.87
H_2O_2	**C12**	77.4	480	6.98 ±0.30	29.66 ±6.05	0.9335 ±0.1663	1.72 ± 0.32	7.93 ±1.08	90.9 ±1.07	249.76 ±5.26
	C2	77.1	500	6.63 ±0.31	31.49 ±2.75	0.8655 ±0.1283	1.45 ± 0.45	6.72 ±1.73	90.09 ±0.84	254.78 ±3.78
	C13	77.5	500	6.82 ±0.67	31.96 ±2.70	0.8836 ±0.1730	1.69 ± 0.59	7.65 ±1.02	90.69 ±1.01	257.56 ±4.98
Consistency	**C2**	76.1	500	6.63 ± 0.31	31.49 ±2.75	0.8655 ±0.1283	1.45 ± 0.45	6.72 ±1.73	90.09 ±0.84	254.78 ±3.78
	C14	76.7	500	7.04 ± 0.37	30.05 ±4.34	0.8141 ±0..136	1.37 ± 0.27	6.94 ±1.07	91.09 ±1.17	249.78 ±6.89
	C15	77.9	510	6.72 ±0.67	28.53 ±4.91	0.8585 ±0.1155	1.37 ± 0.21	7.11 ±1.09	88.66 ±0.62	253.65 ±6.56
	C16	77.1	520	6.56 ±0.45	28.42 ±3.57	0.8483 ±0.1232	1.32 ±0.34	7.01 ±1.23	89.3 ±0.87	248.45 ±7.45
Oleic Acid	**C17**	78.4	490	6.59 ±0.37	25.48 ±2.06	0.7016 ±0.1518	1.07 ± 0.32	6.48 ±0.99	91.17 ±0.53	253.19 ±8.67
	C15	77.9	510	6.72 ±0.67	28.53 ±4.91	0.8585 ±0.1155	1.37 ± 0.21	7.11 ±1.09	88.66 ±0.62	253.65 ±6.56
	C18	75.4	480	7.1 ±0.57	26.56 ±1.77	0.7167 ±0.1479	1.08 ±0.31	6.26 ±1.21	90.09 ±0.84	249.67 ±7.89

Deinking efficiency was calculated using the formula, *DE* = [(*EP-EF*)/(*EP-EB*)] x 100%, where **DE=** Deinking efficiency based on ERIC value (%), **EB=** ERIC value in the absence of ink particles, **EF=** ERIC value after flotation and washing deinking, **EP=** ERIC value of the sample before ink removal (after pulping). In all experiments with chemicals, EB = 21.3 ppm.

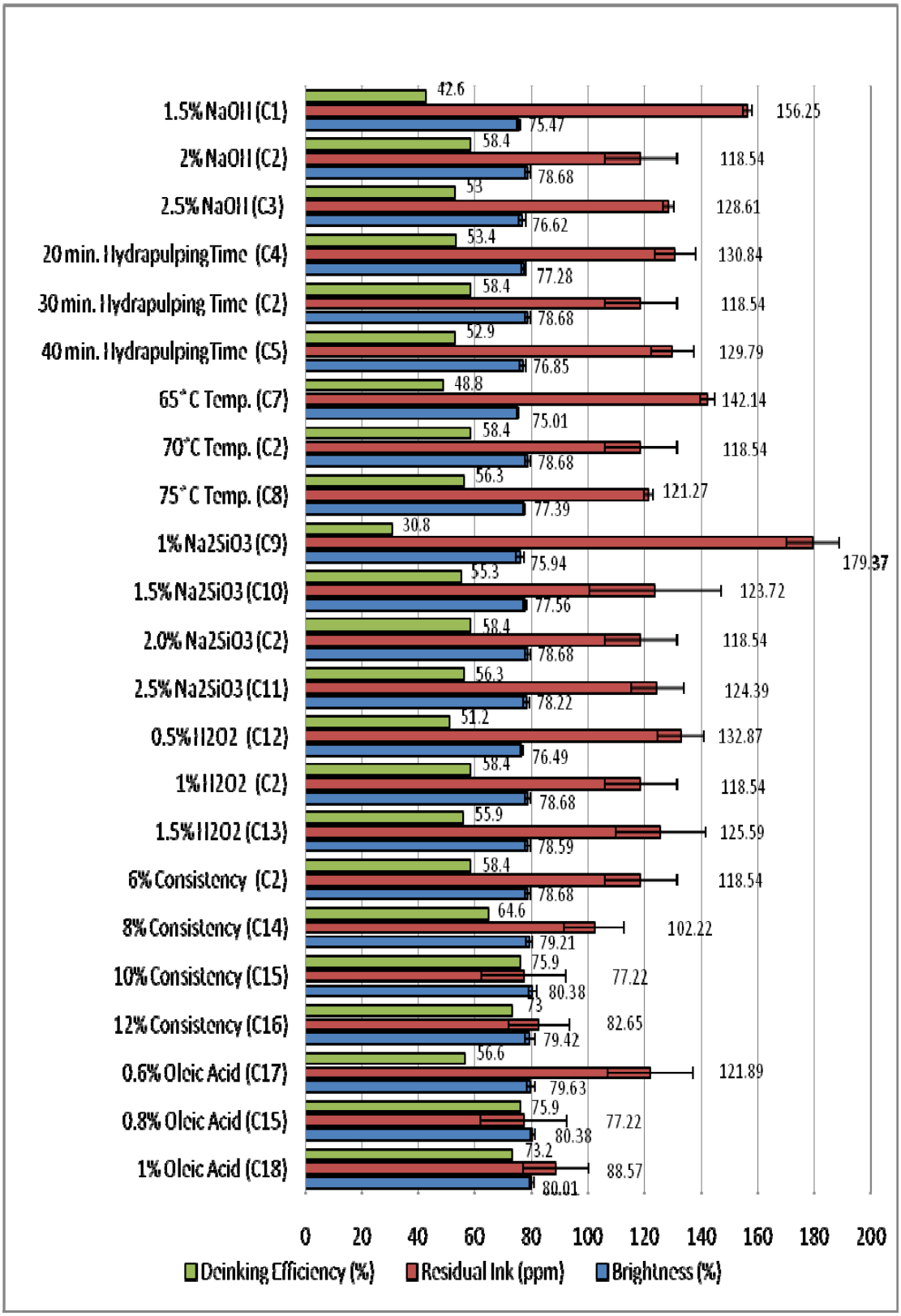

Fig. 1. Optimization of parameters for chemical deinking on the basis of deinking efficiency (%), residual ink (ppm), and brightness (%)

Optimization of Enzymatic Deinking Parameters

Parameters such as the point of enzyme addition, consistency, enzyme dose, and reaction time were optimized for the enzymatic deinking. For each trial, the pH and the temperature of the enzyme were kept at 5.8±0.1 and 50±2°C. Total hydrapulping time was 30 minutes, i.e. the optimized length of time in the case of chemical deinking (Table 2). The hydrapulping time is the total time of mechanical agitation in the hydrapulper, while reaction time referred to the total contact time of enzyme with the pulp. The effects of enzymatic deinking on different pulp and paper properties are shown in Table 4.

Point of enzyme addition

The effect of the point of inoculation of enzyme was evaluated by adding enzyme before hydrapulping (E1), during the hydrapulping (E2), or after hydrapulping (E3) (Table 2). For E1, the torn paper was kept in contact with enzyme and then before hydrapulping the pulp was kept in boiling water for 20 minutes. In the experiment E2, the enzyme was added to torn paper in the hydrapulper and agitated for three rounds. In each round, after every 10 minutes of hydrapulping, agitation was interrupted for 20 minutes. In order to understand the process, hydrapulping time with reaction time, agitation was denoted as A^+, no agitation as A^-, while the numeric value in the subscript denoted the time in minutes. The total reaction time was kept to 90 minutes ($\mathbf{A}^+_{10}+\mathbf{A}^-_{20}+\mathbf{A}^+_{10}+\mathbf{A}^-_{20}+\mathbf{A}^+_{10}+\mathbf{A}^-_{20}$). For condition E3, enzymatic treatment was applied after hydrapulping (Table 2). The maximum deinking efficiency (69.68%) with lowest residual ink count (102.67 ppm) was obtained when enzyme was added in the hydrapulping stage, i.e. E2 (Fig. 2). The importance of mixing for the enzyme action has previously been reported (Zeyer *et al.*1994). Based on above result, this enzyme was added in the hydrapulping stage with interrupted agitation in all the experiments.

Consistency

The effect of pulp consistency was examined in the range of 6 to 14%, and the results obtained indicated that highest deinking efficiency (94.64%) and ISO brightness (78.67%) were achieved when the consistency was kept at 10% (Fig. 2). Further increase in consistency resulted in decreased deinking efficiency and ISO brightness, which could be related to the substrate inhibition or enzyme inadequacy for higher substrate. Fiber-fiber friction increased with pulp consistency; such an explanation seems consistent with earlier findings that enzymatic deinking is more effective at medium consistency as opposed to low consistency (Jeffries *et al.*1994).

Enzyme dose

The selection of the optimal enzyme concentration is important, since excessive enzymes may be detrimental to the fibers and thus affect the strength of the paper and its quality (Lee *et al.* 2007). Experiments were carried out with different doses of enzyme (500 to 2500 IU). For 1500 IU enzyme dose, deinking efficiency and ISO brightness were maximum (94.64% and 78.67%, respectively), and residual ink was lowest (31.95 ppm), but further increase in enzyme dose resulted in reduction in deinking efficiency (Fig. 2). Jeffries *et al.* (1994) reported that high enzyme loading led to a reduction in brightness because of accumulation of enzyme particles on the surfaces of the fibers.

Table 4. Effect of Enzymatic Deinking on the Pulp and Paper Properties

Parameters		Exp. No.	Yield (%)	CSF (ml)	Drainage rate (sec.)	Tensile Index (N.m/g)	Folding endurance	Burst index (kPa.m^2/g)	Tear index (mN.m^2/g)	Opacity (%)	Residual ink (ppm) (EP)#
Point of inoculation	Before HP	E1	79.2	510	6.65 ±0.29	30.31 ±2.71	0.7802 ±0.0987	1.56 ±0.29	6.05 ±0.31	90.42 ±1.04	300.04± 3.56
	During HP	E2	77.9	560	6.21 ±0.21	30.65 ±2.1	0.7856 ±0.1008	1.55 ±0.23	5.95 ±0.54	90.01 ±0.65	301.24± 4.67
	After HP	E3	78.3	540	6.34 ±0.34	31.04 ±1.42	0.8025 ±0.1007	1.60 ±0.34	6.14 ±0.45	89.67 ±0.54	295.95± 6.35
Enzyme dose		E2	77.9	560	6.21 ±0.21	30.65 ±2.1	0.7856 ±0.1008	1.55 ±0.23	5.95 ±0.54	90.01 ±0.65	301.24± 4.67
		E4	78.0	580	6.20 ±0.30	30.14 ±3.98	0.7945 ±0.1023	1.49 ±0.32	5.85 ±0.6	90.6 ±0.53	290.11± 6.61
		E5	77.1	620	5.95 ±0.17	29.31 ±3.64	0.7504 ±0.1039	1.58 ±0.36	5.55 ±0.88	90.1 ±1.01	308.46± 4.78
		E6	76.4	610	6.01 ±0.29	28.65 ±2.87	0.7387 ±0.1230	1.32 ±0.46	5.3 ±0.43	89.34 ±0.43	295.67± 4.87
		E7	75.9	610	5.80 ±0.21	28.09 ±1.65	0.7278 ±0.0782	1.22 ±0.36	5.45 ±0.37	89.06 ±0.67	290.87± 3.98
Consistency		E8	79.4	560	6..31 ±0.20	30.12 ±1.91	.7999 ±0.0972	1.68 ±0.53	5.97 ±0.34	90.76 ±0.78	287.09± 5.37
		E9	78.9	570	6.3 ±0.36	30.56 ±2.87	.8110 ±0.0789	1.65 ±0.65	6.10 ±0.64	90.22 ±0.76	298.65± 5.45
		E5	77.1	620	5.95 ±0.17	29.31 ±3.64	0.7504 ±0.1039	1.58± 0.36	5.55 ±0.88	90.11 ±1.01	308.46± 4.78
		E10	77.6	600	6.14 ±0.34	28.09 ±1.87	0.7345 ±0.1054	1.32 ±0.45	5.45 ±0.54	89.87 ±0.53	307.98± 3.67
		E11	76.8	580	6.2 ±0.18	28.65 ±2.87	0.7456 ±0.0987	1.43 ±0.65	5.40 ±0.45	89.30 ±0.43	300.98± 4.34
Reaction time		E12	79.0	480	6.98 ±0.43	30.87 ±3.54	.8220 ±0.0895	1.70 ±0.65	6.14 ±0.34	90.11 ±0.45	289.98± 2.76
		E13	77.5	540	6.50 ±0.34	30.12 ±2.63	0.8221 ±0.0872	1.65 ±0.45	6.01 ±0.53	89.87 ±0.34	297.45± 3.87
		E5	77.1	620	5.95 ±0.17	29.31 ±3.64	0.7504 ±0.1039	1.58 ±0.36	5.55 ±0.88	90.11 ±1.01	308.46± 4.78
		E14	75.6	600	6.28 ±0.25	28.31 ±2.54	0.7654± 0.1012	1.56 ±0.54	5.67 ±0.56	88.7 ±0.56	298.45± 5.43
		E15	75.2	580	6.38 ±0.28	28.76 ±1.98	0.7332 ±0.1098	1.45 ±0.26	5.43 ±0.23	88.98 ±0.76	301.65± 3.56

# denotes Deinking efficiency was calculated by using the formula described in Table 3.
In all the experiments with enzyme, EB =16.3 ppm

Reaction time

The reaction time for enzyme in the hydrapulper was optimized within the range of 30 minutes to 150 minutes (including 30 minutes for hydrapulping). For the optimization of 30 minutes reaction time, continuous agitation was carried out (A^+_{30}). For the rest of the time variations, the total hydrapulping time was kept equal i.e. 30 minutes (3 rounds of 10 minutes). 60 minutes ($\mathbf{A}^+_{10}+\mathbf{A}_{10}+\mathbf{A}^+_{10}+\mathbf{A}^-_{10}+\ \mathbf{A}^+_{10}+\mathbf{A}^-_{10}$), 90 minutes ($\mathbf{A}^+_{10}+\mathbf{A}^-_{20}+\mathbf{A}^+_{10}+\mathbf{A}^-_{20}+\ \mathbf{A}^+_{10}+\mathbf{A}^-_{20}$), 120 minutes ($\mathbf{A}^+_{10}+\mathbf{A}^-_{30}+\mathbf{A}^+_{10}+\mathbf{A}^-_{30}+\ \mathbf{A}^+_{10}+\mathbf{A}^-_{30}$), and 150 minutes ($\mathbf{A}^+_{10}+\mathbf{A}^-_{40}+\mathbf{A}^+_{10}+\mathbf{A}^-_{40}+\ \mathbf{A}^+_{10}+\mathbf{A}^-_{40}$). The maximum deinking efficiency (94.64%) and ISO brightness (78.67%) were achieved for 90 minutes reaction time. The lowest residual ink count was 31.95 ppm (Fig. 2).

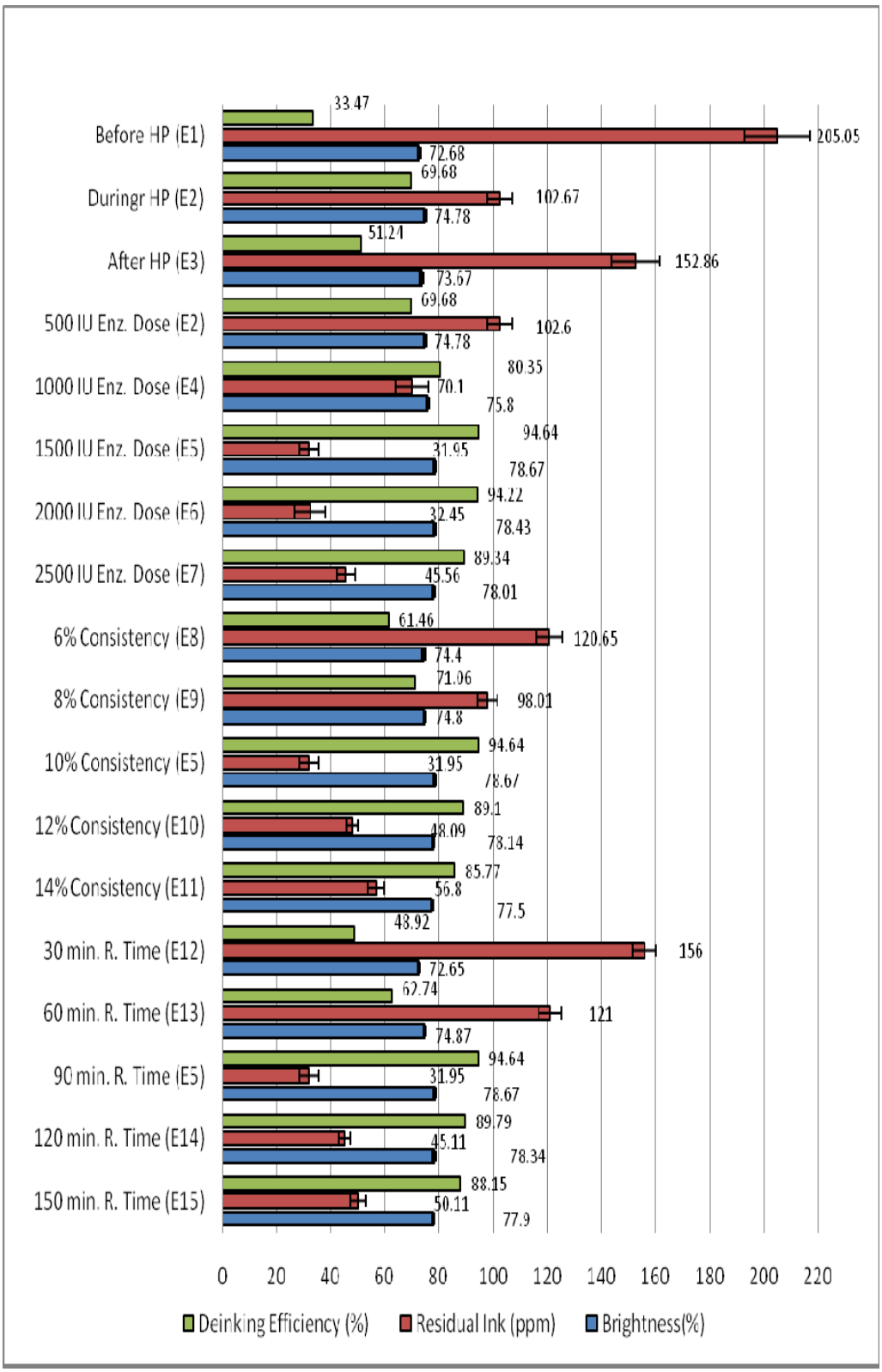

Fig. 2. Optimization of parameters for enzymatic deinking on the basis of deinking efficiency (%), residual ink (ppm), and brightness (%)

Further increase in reaction time resulted in decreased deinking efficiency and ISO brightness. The reason may be redeposition of ink particles on the fiber surface or longer pulping time breaking down detached ink particles, favoring their entry into pits.

Comparison of Chemical and Enzymatic Deinking

A commercial cellulase was compared with conventional chemical deinking of photocopier printed-paper. Deinking efficiency, residual ink, brightness, and yield of optimized conditions are shown in Fig. 3. The optimum conditions for the chemical and enzymatic deinking are summarized in Table 5.

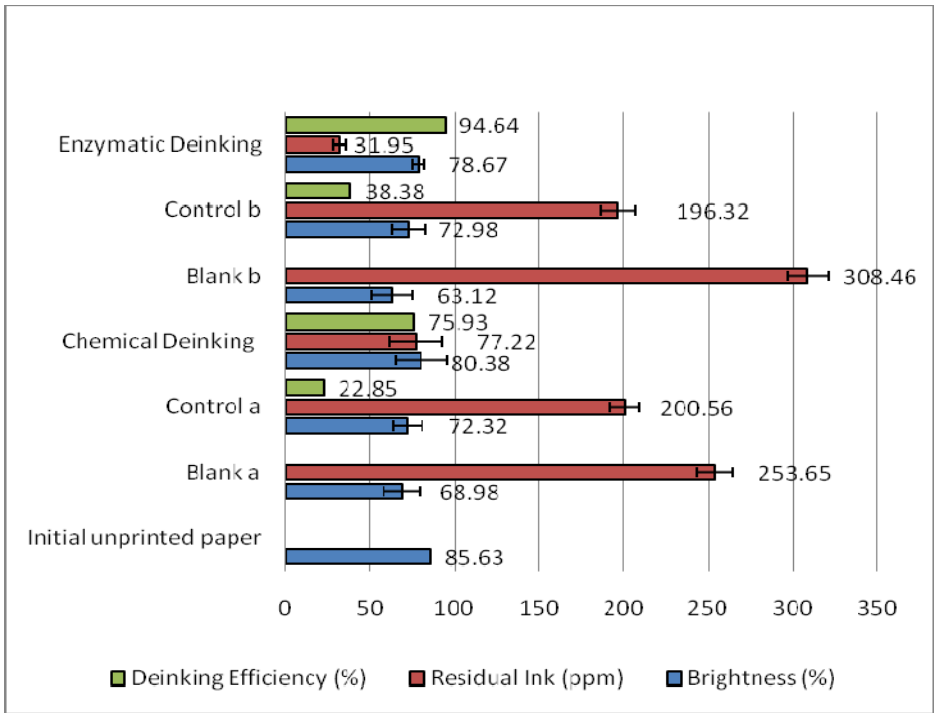

Fig. 3. Comparison of chemical and enzymatic deinking

Brightness

Results of brightness measurements after chemical and enzymatic repulping and flotation are shown in Fig. 3 in comparison to the initial unprinted paper, blank, and control stock. Enzymatically deinked samples were found to be less bright (reduced by 2.1%) than the chemically treated stock. This might be due to (i) dark color of the enzyme, (ii) the addition of hydrogen peroxide during the chemical deinking, or (iii) removal of coating and fillers from the voids and fiber surfaces (Viesters *et al.*1999) as a result of the acidification and/or enzyme treatment followed by their occupation by highly dispersed small size ink particles. It should be noted that the brightness of enzymatically deinked pulp can be further enhanced by use of a post-bleaching stage.

Freeness

Freeness was improved by 21.56%, and consequently drainage time was reduced by 11.45% in the case of enzymatic deinking as compared to chemical deinking (Table 6). It has been proposed that such an increase in freeness is due to selective removal of fine fibres by enzymatic hydrolysis (Park et. al. 2001). Previously also freeness improvement has been attributed to limiting enzymatic action, which preferentially removes fines (Jeffries *et al.*1994; Gubitz *et al.*1998; Lee *et al.*1999; Gliese *et al.*1996) that result in the removal of sufficient hydrophilic material, which in turn improves drainage (Pommier *et al.* 1989). Freeness may also be improved by enzymatic action on small colloidal particles (Grant *et al.* 1990; Young *et al.* 1989; Putz *et al.* 1990).

Table 5. Optimized Parameters of the Chemical and Enzymatic Deinking

Parameters optimized	Chemical Deinking	Enzymatic Deinking
Consistency (%)	10	10
Temperature (°C)	70	50
Hydrapulping Time (min.)	30	30
NaOH (%)	2	NA
Na_2SiO_3 (%)	2	NA
DTPA (%)	0.8	NA
Oleic acid (%)	0.8	0.8
H_2O_2 (%)	1	NA
Enzyme Dose (IU)	NA	1500 IU
End pH (hydrapulping)	10.5	5.8
End pH (flotation)	8.3	6.7
Agitation rate (rpm)	1380	1380
Hydrolysis time (min.)	NA	90
Flotation time (min.)	10	10
Flotation temperature (°C)	40±2	40±2
Deinking efficiency (%)	75.93	94.64

Strength Properties

Table 6 shows values for the strength properties of each pulp treated at the optimum enzyme level with the corresponding control and chemically deinked pulp. The strength properties were compared for deinked pulps obtained as such after the washing stage. The ash content in chemically deinked pulp was higher (2.35%) than the enzymatically deinked pulp (0.9%). Tensile index and burst index of enzymatically treated pulp handsheets were found to be higher, while tear index was lower than those of chemically deinked pulp sheets. It is suggested that enzymatic action resulted in internal fibrillation of fiber as well as some degree of surface fibrillation (compare SEM photographs in Fig.4, where one can observe increased degree of fibrillation in case of enzymatically deinked pulp). This development enhances surface area of fiber on removal of water and hence improves inter-fiber bonding, resulting in increased burst and tensile strength in spite of observed increased freeness. Park *et al.* (2001) earlier reported that strength generally has an inverse relation to freeness in the conventional treatment, but cellulase improved both freeness and tensile strength.

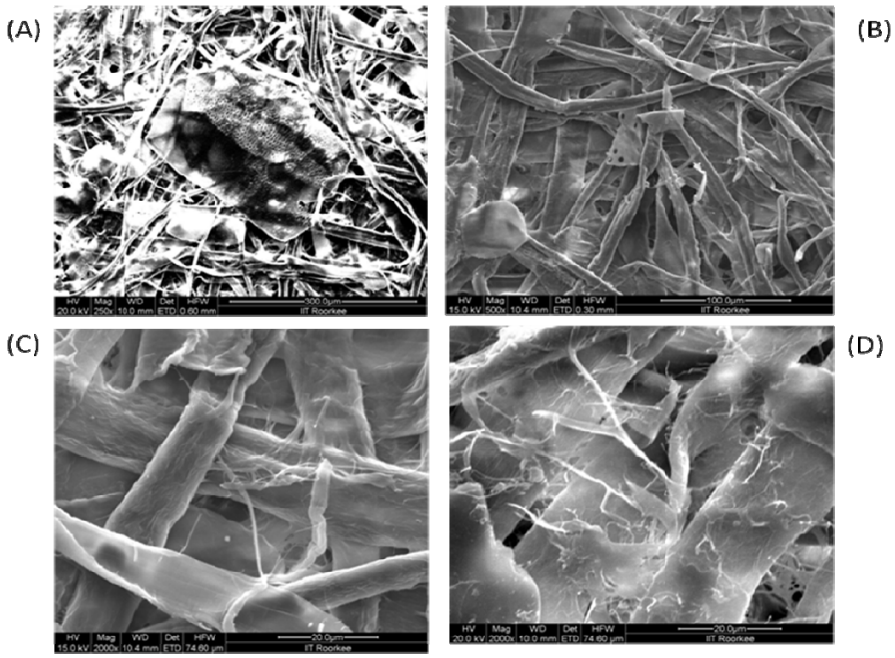

Fig. 4. SEM micrographs showing: toner particles attached with fiber obtained after (A) chemical deinking (500X), (B) enzymatic deinking (500X). Degree of fibrillation on surface of fiber obtained after (C) chemical deinking (2000X), (D) enzymatic deinking (2000X)

Table 6. Comparison of Pulp and Paper Properties

	Initial unprinted paper	Blank (a)	Control (a)	Chemical Deinking	Blank (b)	Control (b)	Enzymatic Deinking
Yield (%)	–	–	80.1	77.9	–	80.2	77.1
CSF (ml)	–	440	480	510	420	470	620
Drainage Time (seconds)	–	7.68 ±0.32	7.23 ±0.32	6.72 ±0.67	7.85 ±0.36	7.49 ± 0.21	5.95 ±0.17
Tensile Index (N.m/g)	45.71 ±2.45	26.45 ±3.22	27.96 ±3.85	28.53 ±4.91	26.65 ±2.33	27.65 ±3.65	29.31 ±3.64
Folding Endurance*	1.1461 ±0.1527	0.7210 ±0.0952	0.7465 ±0.1234	0.8585 ±0.1155	0.7423 ±0.1002	0.7610 ±0.1024	0.7504 ±0.1039
Burst index ($kPa.m^2/g$)	1.44 ± 0.27	1.33 ±0.14	1.34 ±0.14	1.37 ± 0.21	1.33 ±0.19	1.35 ±0.24	1.58 ±0.36
Tear index ($mN.m^2/g$)	5.95 ±0.53	6.30 ±1.2	6.75 ±0.85	7.11 ±1.09	6.23 ±0.95	6.85 ±1.01	5.55 ±0.88

a= for chemical treatment, b= for enzymatic treatment
***** Denotes folding endurance = $\log_{10}$ (number of double folds)

It was thought that the observed increase in freeness was due to selective removal of fine fibres by enzymatic hydrolysis, while strength increased due to enhancement in the hydrogen bonding due to fibrillation of fiber. The increased bonding in turn is responsible for decreased tear index, as now tearing proceeds more and more by breaking

of fibers rather than breaking of fiber-fiber bonds. A similar loss of tear index has also been observed by other researchers (Lee *et al.* 1999; Gliese *et al.* 1996; Vyas *et al.* 2003).

pH

Researchers have reported the use of alkaline conditions for deinking (Franks *et al.* 1995; Vyas *et al.* 2003), but the current work demonstrated that low pH was effective, which was similarly reported by Prasad *et al.* (1992, 1993) and Jefferies *et al.* (1994). Toners are not only associated with cellulose fibers but also with white pigments, fillers, and coating components, such as calcium carbonate. Under acidic condition, the dissolution of the removed calcium carbonate coatings can be improved during the flotation process. It was observed that low pH also helped to decrease the particle sizes of the toner, which subsequently helped the removal of the toner from the surfaces of the paper fibers during the flotation process (Lee *et al.* 2007).

CONCLUSIONS

1. Different parameters for chemical and enzymatic deinking of photocopier waste paper have been optimized. Results of deinking efficiency of photocopier waste paper showed that the enzyme used in the present work (OPTIMASE™ CX 40L) performed better than the conventional chemicals used for deinking.
2. The addition of this enzyme at the hydrapulping stage at 10% consistency would be advantageous for industrial usage.
3. The application of enzymatic deinking improves ink removal efficiency by 24.6% and freeness by 21.6%, with the reduction in drainage time by 11.5% (better machine runnability) with respect to those obtained with chemical deinking.
4. The physical properties, namely burst index and tensile index, improved by 15.3% and 2.7%, respectively, and brightness and tear index were reduced by 2.1% and 21.9%, respectively.

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